Heteropoly Compounds and Their Properties as Catalysts, in Oxidation Reactions and Methanol to Hydrocarbon Process.

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INTRODUCTION

Heteropoly compounds are ionic solids with complex, high molecular weight anions, the latter possessing a minimum of three elements. Although heteropoly compounds possess a variety of structures, those of interest in the present work have anions with cagelike structures, often referred to as Keggin units (Fig. 1).   These have a central metal atom contained within a tetrahedron of oxygen atoms which is itself surrounded by twelve octahedra of oxygen atoms with a second metal atom at each of their centres.   The octahedra overlap and share a portion of their oxygen atoms with each other and with those of the central tetrahedron.   The central metal atom is typically P, Si, As, while the peripheral metal atoms are commonly W, Mo, V, and Ti.

Fortunately, detailed structural information for some of the heteropoly compounds is beginning to become available. One of the most detailed studies was that performed by Brown, Noe-Spirlet, Busing and Levy (1) with X-ray crystallography and neutron diffraction on 12-tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot nH_2O$).   Their work showed that the proton in this heteropoly acid is surrounded by four water molecules only two of which are hydrogen-bonded to the proton at a given time.   The water molecules are, in turn, hydrogen-bonded through their hydrogen atoms to the outer or terminal oxygen atoms of the anions (Fig. 2).

Heteropoly compounds have gained increasing interest in the last few years, largely as heterogeneous catalysts, but also in homogeneous catalysis (for example, refs. 2-6). One of the sources of the interest in the catalytic properties of these solids undoubtedly lies in their multifunctional capabilities.   As a result of variation in their elemental composition, virtually a continuous change in catalytic functions can be achieved, ranging from that associated with Bronsted acidity to that with oxidation catalysis, while the Keggin structure is retained.

While the cation can be shown to influence the catalytic properties in various ways, but principally through changes in both the bulk and surface properties of the heteropoly compound, the present work is primarily concerned with the effect of the anion on the bulk, surface and catalytic properties of heteropoly compounds.   The influence of the anion, and in particular the nature of both the central heteroatom and the peripheral metal atoms, can be seen from the results of a variety of experiments. Hayashi and Moffat (2) have shown that 12-tungstophosphoric acid catalyzes the gas phase conversion of methanol to hydrocarbons at 350°C, for example, while with 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), oxidation predominates.   Pretreatment of the former catalyst with air at 400°C reduces the conversion to hydrocarbons, while the use of helium or hydrogen in the calcination is beneficial to the conversion process.

The dehydration of propanol is catalyzed by a variety of heteropoly acids as $H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$ $H_5PW_{10}V_2O_{40}$ $H_3PMo_{12}O_{40}$ $H_5PMo_{10}V_2O_{40}$ $H_4SiMo_{12}O_{40}$

(5). In the oxidation of methacrolein heteropoly acids $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ have been shown to be more active and selective than $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (6). In the oxidation of acrolein, methacrolein, and isobutyric acid by $H_3PW_xMo_{12-x}O_{40}$, the conversion increases as the value of x decreases, that is as the molybdenum content increases (6). Finally it should be noted that in many of the reactions catalyzed by heteropoly compounds, the existence of the Keggin structure of the anion appears to be a necessary although not a sufficient condition for the efficacy of the heteropoly compounds as heterogeneous catalysts (7).

Although the anion structure and composition are quite evidently of particular importance to the activity of the heteropoly compounds, the nature of the cations cannot be disregarded. Hayashi and Moffat (3) have compared the activity and selectivity of a number of salts of 12-tungstophosphoric acid in the conversion of methanol to hydrocarbons. Of the metal salts employed, Na, Zr, Zn, B, Mg, and Aℓ, the first and the last produced the lowest and highest yields, respectively, of hydrocarbons. The yield of hydrocarbons was shown to increase with decreasing magnitude of charge on the peripheral oxygen atoms of the anion. The ammonium salt of 12-tungstophosphoric acid was found by Hayashi and Moffat (4) to produce significantly higher yields of paraffinic hydrocarbons, as contrasted with the largely olefinic products from both the parent acid and its metal salts.

In the present paper the results from temperature programmed desorption (TPD), photoacoustic spectroscopy in the infrared region (PAS), and semi-empirical (extended Hückel) calculations are presented to demonstrate the relationship between the cation, the anion and catalytic properties of the heteropoly compounds.

METHODS

To conserve space only the briefest description of procedures will be presented. The TPD experiments were carried out on a standard apparatus, described elsewhere (8,9). Both a thermal conductivity detector and a C.E.C. mass spectrometer, the latter attached to the system via a variable leak valve, were used as detectors. PAS-FTIR spectra from 4000-550 cm^{-1} using the were recorded at 5 cm^{-1} resolution on a Bomem DA3.02 Fourier Transform globar source and KBr beamsplitter. The photoacoustic detector module, supplied as a standard accessory by the manufacturer, was used with minor modifications (10).

RESULTS AND DISCUSSION

The TPD of 12-tungstophosphoric acid exhibits two peaks (Fig. 3), one centred at 473°K (Peak 1) with an unresolved shoulder on the high temperature side, the other a very broad asymmetrical peak centred around 773°K (Peak 2), both due entirely to water as shown from mass spectrometry. The magnitudes of peaks 1 and 2 corresponded to 1.3-1.4 and 6.5 water molecules per Keggin Unit (KU), respectively. Outgassing at 463 or 593°K essentially removed peak 1 but had no effect on peak 2. No peaks were observed after outgassing at 723°K. It should be noted that copious quantities of water were evolved from the unpretreated HPW at room temperature when a stream of helium was passed through the sample. Water desorbed during outgassing at 463 or 593°K could be replaced by contacting the acid with water vapour at 298°K, but after outgassing at 723°K it was not possible to restore the original TPD behaviour.

The heteropoly acids, 12-molybdophosphoric acid and 12-tungstosilicic acid, as with HPW, displayed two peaks (1 and 2) both due to water (not shown). In addition a very sharp peak (peak 3) was evident on the high temperature side of

peak 2. While the positions of the peaks for HSiW were similar to those with HPW, those for HPMo were found at approximately 373, 673, and 723°K, for peaks 1, 2, and 3, respectively. The importance of the peripheral metallic element of the anion in determining the TPD behaviour is evident.

The position of peak 1 for each of the acids reported here is consistent with the type of multiple hydrogen bonding interactions between the acid and molecular water, as found by Brown et al (1). Since the position of peak 1 depended strongly on the peripheral element of the anion, it appears that such interactions occur externally to the Keggin Unit, consequently largely shielded from influence by the central atom of the anion. It appears the peak 2 must be associated with a deprotonation of the catalyst, the protons combining with anionic oxygen to emerge as molecular water. X-ray diffraction analysis of HPW, which had been pretreated at 723°K suggested that decomposition of the structure had not occurred, in spite of the loss of anionic oxygen.

The PAS spectrum of HPW after pumping at room temperature displays a featureless background absorption which extends across the range from approximately 2000 to 4000 cm^{-1} (Fig. 4). The broad band at 3200 cm^{-1} and the more intense and narrow band at 1710 cm^{-1} may be attributed to molecular water and protonated water. The bands below 1100 cm^{-1} are characteristic of the Keggin Unit. After heating with evacuation at various temperatures up to 450°C, the band at 1710 cm^{-1} decreases and shifts to 1640 cm^{-1}, the bending vibration of lattice water. The band at 1080 cm^{-1} is assigned to the triply-degenerate asymmetric stretching vibration of the central phosphate tetrahedron, while that at 980 cm^{-1} may be attributed to a stretching vibration of the bonds between tungsten and the outer oxygen atoms. Although at 450°C bands associated with the anion structure have diminished somewhat in intensity it is apparent that the structure remains essentially intact.

The twelve octahedra surrounding the central tetrahedron in the Keggin unit can be divided into four compact tritungstate groups, $W_3O_3^{-8}$, resulting from the edge sharing of three WO_6 octahedra (11) (Fig. 5b). The three octahedra in each such group have one common oxygen atom, which is also part of the inner tetra-hedron in the heteropoly anion, and three other oxygen atoms are each shared by two octahedra to form the edge-shared unit. In $W_3O_{13}^{-8}$ there are three terminal and three bridging oxygen atoms on the outer surface of the unit, when viewed as a fragment of the heteropoly anion. The central tetrahedron may then be attached to produce the $XM_3O_{16}^{-n}$ species (Fig. 5a), where X refers to the central atom and M the peripheral metal atom. The use of this fragment to simulate the heteroply anion in semi-empirical extended Hückel calculations provided a convenient means of evaluating the effect of charges in both the central and the peripheral atom.

The effect of changes in the central atom and the peripheral atoms of the Keggin structure may be observed from calculations on $PW_3O_{16}^{-9}$(PW), $SiW_3O_{16}^{-10}$ (SiW) and $PMo_3O_{16}^{-9}$ (PMo) (Fig. 6). The net atomic charges on the outer atoms of the former two species are similar, while those on the fragment containing molybdenum are considerably more negative. In addition, the partitioned energies for the M-O (outer) bond on PW and SiW are approximately the same, that on PMo is considerably smaller. Evidently, a change in the central atom has little effect on either the atomic charges of the outer oxygen atoms or the partitioned energies of the bonds formed by these atoms with the peripheral metal atoms. In contrast, substitution of the peripheral atoms, with the central atom fixed, produces substantial changes in the two properties.

The results of these calculations together with the available experimental data are consistent with the conclusion that Bronsted acidity increases as the

magnitude of the negative charges on the outer oxygen atoms of the heteropoly fragment decreases, while the activity in oxidation reactions can be correlated with the energy associated with the bond between the outer oxygen atom and the peripheral metal atom.

It appears reasonable as a first approximation to assume that the protons in the heteropoly compounds are interacting primarily with the outer oxygen atoms of the anion structure. The acid strength, being directly dependent on the mobility of the protons, should then be inversely proportional to the magnitude of the negative charge on these oxygen atoms. In the oxidation processes involving heteropoly compounds, it may be reasonably assumed, again as a first approximation, that the activity of these catalysts is related to the case with which the most immediately available oxygen atom can be removed from the anion. The partitioned energy of the bond associated with the peripheral metal atoms and the outer oxygen atoms of the anion would therefore appear to fill this role.

ACKNOWLEDGEMENTS

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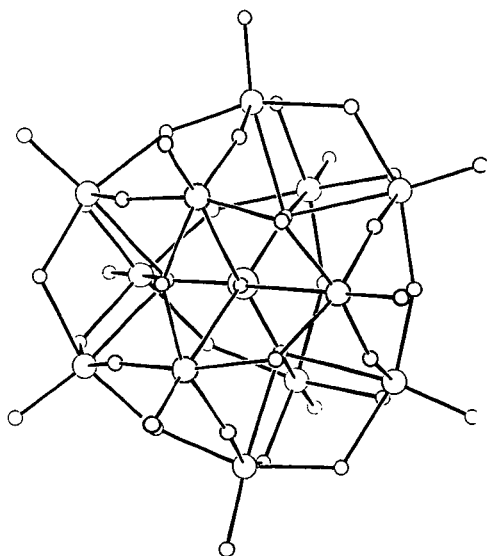11. D.L. Kepert, in Comprehensive Inorganic Chemistry, J.C. Bailar (Ed.) Vol. 4, Chapt. 51, Pergamon, New York, 1973.

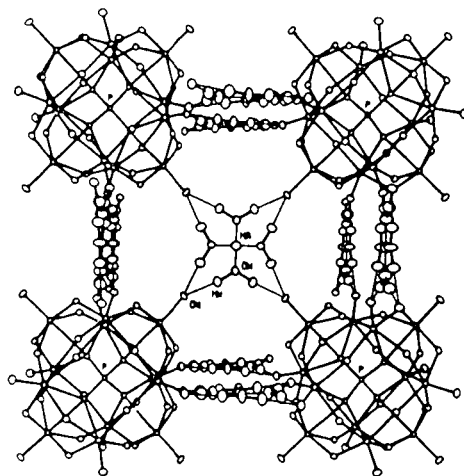Figure 1   Anion of $SiMo_{12}O_{40}^{-4}$

Figure 2   Arrangement of cations, water, and anions in 12-tungstophosphoric acid.
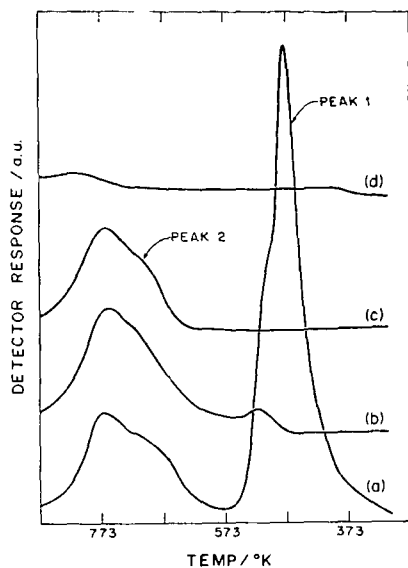
Figure 3   *Temperature Programmed Desorption spectra of 12-tungstophosphoric acid after pretreatment temperatures of (a) 298°K, (b) 463°K, (c) 593°K, (d) 723°K (9).*
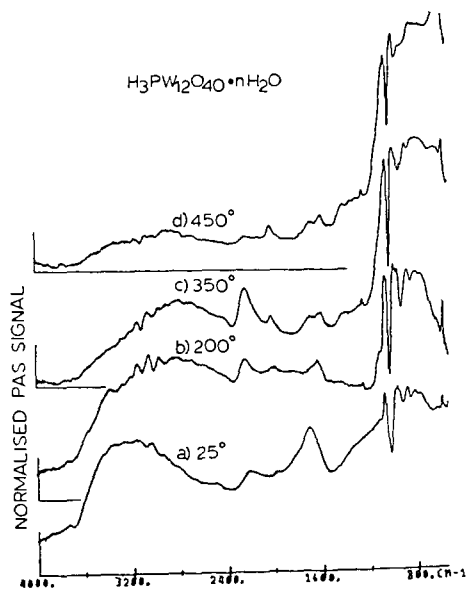

Figure 4   *Photoacoustic spectra of 12-tungstophosphoric acid after heating with evacuation at various temperatures (10).*
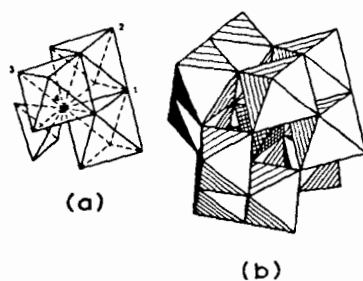
Figure 5   (a) Fragment $XM_3O_{16}^{-n}$ of heteropoly anion.
             (b) Heteropoly anion showing position of fragment.
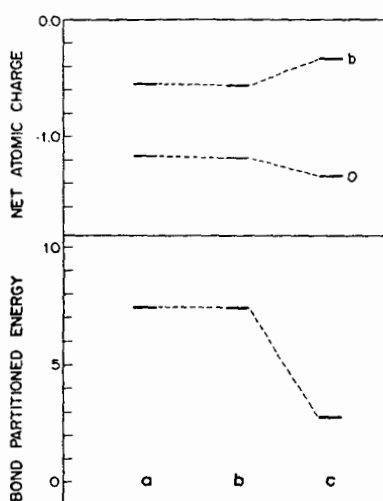

Figure 8   Results of extended Hückel calculations of net atomic charges on
             bridging (b) and outer (o) oxygen atoms and partitioned
             energies for the M-O (outer) bond.